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Comparative Effect of Various Photo-Substituted Transition Metal Complexes Derived from Hexaminecobalt(III) Chloride on Thermal Properties of Polyaniline Nanocomposites

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ABSTRACT

The present paper reviews the comparative effect of different transition metal complexes derived from hexaminecobalt(III) chloride metal complex on the thermal properties of polyaniline nanocomposites. These metal complexes are obtained through photo-substitution route in which some of the amine ligands of the hexaminecobalt(III) chloride metal complex are photochemically substituted by different organic ligands like 1,10 phenenthroline, pyrazine and imidazole. It is observed that the metal complexes thus synthesised containing both organic and inorganic moieties enhance the thermal stability of polyaniline to a great extent as compared to simple hexamine metal complex filled nanocomposite. However, as far as the role of different incorporating organic ligands of metal complexes on the thermal properties of polyaniline nanocomposites are concerned, there seems to be little or no effect.

Introduction

Very little literature is available where transition metal complexes have been used as fillers in the polyaniline matrix for the formulation of nanocomposites. However, their use is justified, since they possess electrical, optical, catalytic and magnetic properties which may be incorporated in polymer matrices for the desired device fabrication. For example the metal complexes potassium ferrocyanide $K4[Fe(CN)_6]$ and copper bisglycinate $[Cu(gly)_2]$ has been found to increase the thermal stability of polyaniline for high temperature application purposes [1, 2]. The PANI/ferricyanide composite has been used as efficient adsorbent for the removal of Cu(II) from aqueous solution [3]. The composites of PANI with nickel bisacetylacetonate and zinc bis(8-hydroxyquinolate) are observed to be potent materials for electronic and optoelectronic devices such as light emitting diodes, solar cells and other semiconducting devices [4,5]. Polyaniline/magnesium chromate ($MgCrO_4$) composite was found to possess humidity sensing behaviour [6], etc. Recently photo-substituted transition metal complexes have been used as an entirely new kind of filler in the polymer matrices. These are obtained as a result of photo induced ligand exchange reaction between a photo reactive transition metal complex and a chosen ligand. Our research group have observed the prospectus of this kind of filler on the electrical, optical, thermal and photocatalytic properties of polyaniline, polypyrole and polythiophene polymers [7-13].

Experimental

Synthesis of photo-substituted metal complex nanoparticles

The different photo-substituted metal complexes were synthesised by irradiating a 1:2 ratio solution mixture of $[Co(NH_3)_6]\ Cl_3$ metal complex and different organic ligands like 1, 10 phenenthroline, pyrazine and imidazole. The irradiation was carried under OSRAM photo lamp for half an hour. The irradiation caused change in the colour of the solution in each case due to photo-substitution and therefore subsequent change in the ligand environment around the Co(III) metal ion. The solution mixture was concentrated on a water bath and then allowed to cool under ambient conditions, when the bright coloured crystals of the photo-substituted metal complexes separate out. The crystals were isolated and dried in an oven at a temperature of 25–30 °C. The different synthesised photo-substituted metal complexes were finally reduced in size by RETSCH planetary PM 100 high energy ball mill to obtain nano particles. The balls used were of zirconium with 10 mm size and weigh 0.85 g. A 1:5 weight ratio was fixed between the sample and balls (approx. 10 balls per 2 g of the sample). The sample was milled for 12 h with fixed time intervals of 5 min at a rotational speed of 450 rpm

Synthesis of PANI-metal complex nanocomposites

The different synthesised photo-substituted metal complex nanoparticles were incorporated into the PANI matrix during its chemical polymerisation reaction by ammonium persulphate as oxidising agent in non-aqueous DMSO medium. A 1:1 ratio between the aniline monomer and the photo-substituted metal complex was fixed. To precooled 1 ml distilled aniline in 10 ml of 5 N HCl solution in DMSO, 1.0 g of synthesised photo-substituted metal complex nano powder was added in each case with continuous stirring to form a uniform dispersion. The mixture was sonicated for half an hour to keep the photo-substituted metal complex nanoparticles homogenously suspended. To this dispersion 1.2 g of ammonium persulphate dissolved in 10 ml of DMSO solution was added drop wise at 10 °C with vigorous stirring for a period of 15 min. The slow stirring was then continued for 24 h at a constant temperature of 10 °C for polymerisation reaction to take place. After 24 h a thick dark green mass was formed. This was isolated as precipitate by centrifugation and washed with acetone several times.

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The precipitate was collected over filter paper and dried in an oven at a temperature of about 30–40°C.

Results and Discussion

Comparison of systems with respect to thermal stability

To start with, the thermal stability of all the synthesised nanocomposites was found to be higher than pristine PANI. This is attributed to the occurrence of stronger interaction between the photo-substituted metal complex nanoparticles and the PANI chains which restrict their motion against the thermal degradation. Pristine PANI shows thermal stability up to 600 °C only, whereas this temperature extends to about 800 - 1000 °C in case of all nanocomposites. The different PANI nanocomposites contain about 30-43% residual mass at 600 °C while as there is only 15% residue left in case of pure PANI at the same temperature. The highest thermal stability is observed in PANI nanocomposite containing imidazole as exchange ligand while as the thermal stability was found to be minimum in case of nanocomposite having simple hexamine metal complex. The organic ligand containing photoadducts increase thermal stability of nanocomposites to a great extent as compared to simple hexamine metal complex filled nanocomposite. This is probably due to the compatible nature of organic ligands with the PANI chains and their large size which increases the magnitude of interactions. However, as far as the effect of different exchanging ligands on the thermal stability is concerned, there seems to be little or no effect. The comparison of thermal stability of different nanocomposites of PANI having different filler metal complexes is shown in table 1:

Table 1. Comparison of thermal stability of different PANI nanocomposites

Systems	Incorporating ligand	Thermal Stability Temperature	Residue left at 600 °C
Pristine PANI	-	600 °C	15%
(System I) PANI/$[Co(NH_3)_6]Cl_3$ nanocomposite	-	800 °C	30%
(System II)PANI/$[Co(NH_3)_4(C_{12}H_8N_2)]Cl_3 .5H_2O$ nanocomposite	1, 10 Phen.	862 °C	39%
(System III) PANI/$[Co(NH_3)_3(C_4H_4N_2)_3]Cl_3$ nanocomposite	Pyrazine	Incomplete	31%
(System IV)PANI/$[Co(NH_3)_4(C_3H_4N_2)_2]Cl_3$ nanocomposite	Imidazole	Incomplete	43%

The Thermogravimetric curves showing mass loss with temperature of PANI and its different nanocomposites is shown below in fig.1.

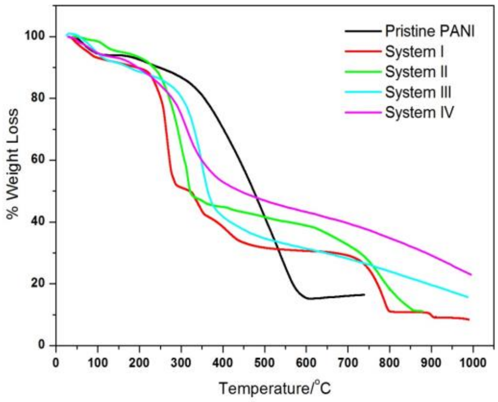

Fig.1. TG curves of pristine PANI and its different nanocomposites (Systems).

Conclusion

From the above discussion it is concluded that the thermal stability of all nanocomposites has enhanced significantly as compared to pristine PANI. The presence of different organic incorporating ligands in nanocomposites show little effect on thermal property with respect to each other but has a considerable effect when compared to pristine polymer and with the nanocomposite containing simple hexaminecobalt(III) chloride metal complex. This is probably due to the compatible nature of organic ligands with PANI chains and their large size which increases the magnitude of interactions.

References

[1]Rather, M.S., Majid, K., Wanchoo, R K., & Singla, M.L. (2014). Role of photoadduct of $K_4Fe(CN)_6$ and $C_3H_4N_2$ in improving thermal stability of polyaniline composite. *Journal of Thermal Analysis and Calorimetry*, *117*(2), 611-619.

[2]Rafiqi, F.A., Rather, M.S., & Majid, K. (2013). Doping polyaniline with copper bisglycinate $[Cu(gly)_2]$-Synthesis, characterization and thermal study. *Synthetic Metals*, *171*, 32-38.

[3]Rafiqi, F.A., & Majid, K. (2015). Removal of copper from aqueous solution using polyaniline and polyaniline/ ferricyanide composite. *Journal of Environmental Chemical Engineering*, *3*(4), 2492-2501.

[4]Rafiqi, F.A., & Majid, K. (2016). Synthesis, characterization, luminescence and magnetic properties of composite of polyaniline with nickel bisacetylacetonate complex. *Polymer Science Series B*, *58*(3), 371-383.

[5]Rafiqi, F.A., & Majid, K. (2016). Synthesis, characterization, photophysical, thermal and electrical properties of composite of polyaniline with zinc bis(8-hydroxyquinolate): a potent composite for electronic and optoelectronic use. *RSC Advances*, *6*(26), 22016-22025.

[6]Machappa, T., & Prasad, M. A. (2012). Humidity sensing behaviour of polyaniline/magnesium chromate ($MgCrO_4$) composite. *Bulletin of Materials Science*, *35*(1), 75-81.

[7]Rather, M.S., Majid, K., Wanchoo, R.K., & Singla, M.L. (2013). Nanocomposite of Polyaniline with the photoadduct of potassium hexacyanoferrate and pyridine ligand: Structural, electrical, mechanical and thermal study. *Synthetic Metals*, *179*, 60-66.

[8]Najar, M.H., & Majid, K. (2013). Synthesis, characterization, electrical and thermal properties of nanocomposite of polythiophene with nanophotoadduct: a potent composite for electronic use. *Journal of Materials Science: Materials in Electronics*, *24*(11), 4332-4339.

[9]Najar, M.H., & Majid, K. (2015). Enhanced photocatalytic activity exhibited by PTh/ $[Fe(CN)_3(NO)(bpy)]\cdot 4H_2O$ nanocomposite fibres via a synergistic approach. *RSC Advances*, *5*(130), 107209-107221.

[10]Najar, M.H., & Majid, K. (2014). Nanocomposite of polypyrrole with the nanophotoadduct of sodium pentacyanonitrosylferrate (II) dihydrate and EDTA: A potential candidate for capacitor and a sensor for HF radio wave detection. *Synthetic Metals*, *198*, 76-83.

[11]Moosvi, S.K., Majid, K., & Ara, T. (2016). Synthesis and characterization of PPY/K $[Fe(CN)_3(OH)(en)]$ nano composite: Study of photocatalytic, sorption, electrical, and thermal properties. *Journal of Applied Polymer Science*, *133*(23), 43487-43498.

[12] Moosvi, S. K., Majid, K., & Ara, T. (2016). Synthesis and characterization of PTP/K[Fe $(CN)_3$(OH)(en)] nanocomposite: study of thermal, electrical and photocatalytic properties. *Journal of Materials Science: Materials in Electronics*, *27*(7), 6891-6901.

[13] Moosvi, S. K., Majid, K., & Ara, T. (2016). Studying the electrical, thermal, and photocatalytic activity of nanocomposite of polypyrrole with the photoadduct of $K_3[Fe(CN)_6]$ and diethylenetriamine. *Materials Research*, *19*(5), 983-990.